

## **Response to RC1:**

*The authors describe first measurements and the spectroscopic characterization of a modified Chernin-type multi-pass cell, which has been designed for wavelengths in the IR and THz region. The multipass cell has been set up as part of the detection equipment of the CHamber for Atmospheric Reactivity and Metrology of the Environment (CHARME) in Dunkirk. The combination of this type of multipass cell and a low-pressure atmospheric chamber is novel, and the data presented inspire confidence in the method.*

First of all, we would like to thank RC1 for their thorough and meticulous reading of the manuscript which has allowed us to significantly improve the quality of our article. We really appreciate the trust he has placed in our measurements and interpretation. In addition, it is very important for us that he noticed the novelty of our approach with the first high-resolution THz measurements at low pressure in an Atmospheric Simulation Chamber (ASC) such CHARME.

*The cell enables path lengths between 120 and 480 m (540 m) in the IR and between 120 m and 280 m in the THz region. Proof-of-principle measurements have been performed with N<sub>2</sub>O and O<sub>3</sub> whose mixing ratios were established. While the sensitivity of the method for those species is modest, its selectivity is a strength, enabling the potential to study less common (polar) VOCs in the future. While the authors address detection limits, applicability of the detection approach, its selectivity and suitability for kinetic studies based on the time resolution during an O<sub>3</sub> reactivity study, I am missing a general comparison with other methods and a classification of the method among other (spectroscopic) approaches in different wavelength regions.*

We agree with the reviewer: the main weakness of the THz method is, for the moment, a modest sensitivity for trace gas monitoring compared to several IR and UV photonic techniques but this weakness is counterbalanced by its selectivity at low-pressure when the rotational linewidths are Doppler limited. Always in agreement with the reviewer, the second advantage of the THz monitoring is the capability to detect *a priori* all the polar atmospheric VOCs and to unambiguously discriminate them with their rotational signatures which would be difficult with vibrational IR and electronic UV bands measured at lower resolution. Finally, due to the capabilities of the RF synthesizer driving the AMC THz source, the acquisition times (typically hundreds of ms) are short and a time-resolved quantification providing kinetic parameters is also possible and simplified by using the THz electronic sources (Omar et al., 2015).

RC1 regrets the absence of a general comparison with other methods and a classification of the method among other (spectroscopy) approaches in different wavelength regions. It is true that there is no specific paragraph dedicated to this type of comparison but, nevertheless, the advantages and disadvantages of THz monitoring compared to other photonic techniques are discussed at different places in the discussion and in the conclusion:

- In the last paragraph of section 3.1, the THz selectivity is compared with the IR one: “*the THz rotational linewidth is estimated to be  $3.4 \times 10^{-4} \text{ cm}^{-1}$  (HWHM), around 300 times smaller than the IR rovibrational linewidth highlighting the excellent selectivity of the THz spectroscopy compared to the IR one due to a weaker Doppler broadening.*”
- The first part of section 3.2 is a general comparison of the advantages and disadvantages of the THz rotational spectroscopy compared to IR rovibrational spectroscopy:

*“Compared to IR rovibrational spectroscopy, rotational THz spectroscopy presents ..... and a time-resolved quantification providing kinetic parameters is also possible and simplified by using the THz electronic sources (Omar et al., 2015).*

*Despite these different advantages, ..... These standing waves strongly affect the baseline and the measured line profiles as observed in Fig. 4a”*

- Finally in the conclusions section, the specificities of the THz monitoring compared to other techniques are again mentioned:

*“The THz monitoring of atmospheric compounds presents some specificities in comparison with other spectroscopic techniques: As example, the measurements of the rotational lines of the most abundant isotopomers of N<sub>2</sub>O highlight the exceptional selectivity of the technique which should be able to detect anomalous isotopic fractionation. Moreover the rotational absorbance allows an absolute quantification of the absorbing compound without standard of calibration. The demonstration was performed on stable N<sub>2</sub>O and reactive O<sub>3</sub> greenhouse gases. According to the measured S/N ratio, the reached detection thresholds are limited to few tens of ppmv due to the baseline oscillations involved by numerous standing waves occurring in MULTICHARME.”*

In order to take into account the remarks of RC1, additional elements have been added in the manuscript:

-At the end of the subsection 3.2.1:

*“Finally the discrimination of the N<sub>2</sub>O isotopomer rotational lines (especially the lines of <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O and <sup>14</sup>N<sup>14</sup>N<sup>16</sup>O on Fig. 6a) highlights the exceptional selectivity of the THz rotational spectroscopy. Indeed, when the measurements are performed at low pressure (typically stratospheric pressures) the linewidths converge to the Doppler limit. For molecules such as N<sub>2</sub>O, the Doppler linewidths, proportional to the line frequencies, typically vary from hundreds of kHz in the THz domain to hundreds of MHz in the IR and to several GHz in the UV visible. No doubt that THz high-resolution monitoring exhibits a significantly better selectivity compared to the IR/UV. In complex chemical mixtures studied in ASC, the THz method allows to observe and resolve individual molecular signatures even for compounds with close molecular structures (isomers, conformers, isotopomers...). Moreover the high-resolution THz method strongly limits the problem of interference substances in the gas monitoring. With photonic detection in the IR/UV spectral domain, it is generally not possible to resolve individual rovibrational or rovibronic transitions with the typical instrumental resolutions (e.g resolutions of FTIR spectrometers coupled to ASC are limited to few GHz) and some corrections due to interferences with other species have to be taken into account in the trace gas quantification (Harris et al., 2020).”*

-At the end of the subsection 3.2.2:

*“In order to determine the Limit of detection (LOD), we have considered the baseline oscillations as our detection noise and the LOD as the concentration obtained with a signal to noise (S/N) equal to 1. Both for N<sub>2</sub>O and O<sub>3</sub>, the S/N of Fig. 7 are estimated to 15 by taking as signal, the maximum amplitude of the rotational line and as noise, the maximum of the amplitude of the residual away from the line. Therefore LOD of around 75 ppmv and 15 ppmv may be estimated respectively for N<sub>2</sub>O and O<sub>3</sub>. These LOD are slightly lower than the mixing ratio errors obtained with the uncertainties on the fitted area. For N<sub>2</sub>O, the LOD obtained by THz spectroscopy in this study are more than three orders of magnitude larger than the LOD on the strongest mid-IR rovibrational bands by Tunable Diode Laser Spectroscopy (TDLAS) even with measurements at low-pressure (Hoor et al., 1999). With the THz method, for instance the LOD is limited to 15 ppmv. Using the Incoherent BroadBand Cavity-Enhanced Absorption Spectroscopy in the visible domain, a LOD of 120 ppbv was obtained in the Dunkirk ASC at atmospheric pressure (Wu et al., 2014). In order to improve the sensitivity of the THz method, we have to correctly model the baseline and to remove its variations due to multiple interfering stationary waves in MULTICHARME. A work is under progress in this goal.”*

-In the conclusion:

*“This step is required to improve the sensitivity of the method in order to reach subppmv LOD for most of small polar atmospheric molecules showing intense rotational transitions at THz frequencies. We have also to think about the possibility to couple in the future a THz cavity-ringdown spectrometer to CHARME (Hindle et al., 2019), by this way, we hope to be competitive with IR and UV-visible techniques in terms of LOD.”*

***The authors discuss some advantages and drawbacks of their approach. They also describe experimental difficulties and how they were overcome, however, more attention to detail, e.g. in the establishment of the LOD or in the discussion of systematic errors, would be helpful.***

The sensitivity of MULTICHARME is limited by the complex and strong baseline variations observed at THz frequencies caused by multiple standing waves. To evaluate the LOD we quantify the amplitude of the recorded molecular signal and the amplitude of the baseline variations “noise”, both after normalization (sample spectra)/(ref spectra). The baseline variation is determined either by comparing two spectra with an empty measurement cell, or examining a portion of a spectra with no molecular transition. The LOD is then determined by an experimental data close to that limit, weak trace absorption whose concentration is extrapolated by the S/N to give the LOD. The LOD then corresponds to the concentration that would give  $S/N = 1$ .

As it was mentioned previously, in order to determine the LOD, we have considered these baseline oscillations as our detection noise and therefore our LOD is the concentration obtained for a  $S/N = 1$ . The effect of the baseline oscillations is now clearly visible with the residuals provided in Fig. 7 as suggested by Reviewer 1 and the description of the fitting process in the new Fig. S5 of the Supplement. As example, with the two THz lines shown in Fig. 7 exhibiting a S/N around 15 if we take as signal, the maximum amplitude of the rotational line and as noise, the maximum of the amplitude of the residual away from the line. So, we can estimate the LODs of around 75 ppmv and 15 ppmv respectively for  $N_2$  and  $O_3$ . In the article, in Fig. 7, we have also determined systematically the errors on the fitted area and consequently the errors on the associated mixed ratio (ex: Fig. 7a,  $\pm 160$  ppmv; Fig. 7b,  $\pm 22$  ppmv). These errors are slightly superior to the LODs. We hope that the additional explanations in subsection 3.2.2 allow the reader to better understand our approach concerning the LOD and the systematic errors determination. The sensitivity improvement requires right now to correctly model the baseline variation due to standing waves, this work is under progress and will be the subject of a future publication.

***The overall presentation of the work is well structured and clear, however, in several places some confusion may arise due to the wording used. The authors give sufficient credit to related work and with a few exceptions most references appear appropriate.***

One more time, we are grateful to RC1 for its careful reading. We have taken into account all its suggested corrections concerning several bad wordings. As asked by the reviewer 1, we have improve several sentences:

- L20. The sentence: “Moreover, a THz monitoring at low pressure of the ozone decay in the chamber has been performed” is replaced by “At low pressure the ozone concentration was continuously monitored and its decay characterized. »
- L25.26 The sentence: “ However, the sensitivity of the THz monitoring needs to be improved to reach atmospheric trace levels. For this purpose, it is necessary to fully understand the origin of the observed baseline variations caused by the complex multiple standing waves present in MULTICHARME.” is replaced by “Right now, the accessible detection levels for both compounds are not sufficient to detect both compounds at atmospheric concentrations. A correct baseline

*modelisation in order to remove its variations due to multiple interfering stationary waves in the Chernin cell is required.*”

- **L142-144. Improve this sentence. To the accuracy of what parameter does the value of  $10^{-7}$  refer to? The wavelength range was calibrated using the Burleigh wavemeter with a specific accuracy? Can you give an absolute value?**

$10^{-7}$  refers to the relative accuracy on the wavelength measurement  $\frac{\Delta\lambda}{\lambda}$ . Yes the wavelength range was calibrated using the Burleigh wavelength-meter with its specific accuracy. The sentence has been replaced by:

*Once the laser was adjusted for the desired operating range, a wavelength calibration was performed (Burleigh WA-1500) with an accuracy better than  $4 \times 10^{-3} \text{ cm}^{-1}$ .*

- **L199-201. Rephrase – these sentences are rather casual and should be more factual.**

We propose a new sentence: *“Reaching a pathlength of 280 m with an amplified frequency multiplication chain which is highly divergent source is a significant improvement compared commonly used setups. Extending the pathlength further should be possible for higher frequencies or with more powerful THz sources.”*

- **L382-385. Split the sentence “The concentration decrease was fitted...” into two or three sentences. What is meant by “...a fit weighted on the estimation of the limit of detection”? This is not clear. The LOD was estimated based on a signal to noise ratio of 1; the authors should say more here. Explain better how the maximal amplitude of the baseline oscillations was determined. Over what spectral region, for what time in the measurement series. What was the maximal signal, S? The integrated absorbance or the max value of the absorbance. In the caption of Fig 8. The authors refer to the “absorbance area”. This is not clear to me. L386. The LOD should be properly stated; i.e.  $50 \pm ??$  ppmv. ... “we are very close to this limit” is too casual. What is the acquisition time for this LOD, is it 3 min?**

We use a weighted fit when the assumption of a constant variance of the errors is not respected. The weighting allows to improve the fit. The idea is simple, we give less weight to the less precise measurements and more weight to more precise measurements when estimating the unknown parameters in the model. With the Origin software, in the Levenberg Marquardt fitting process, we have chosen to perform an exponential fit weighted on the LODs considered as instrumental errors i.e. a weight equal to the  $\text{LOD}^{-2}$  (see <https://www.originlab.com/doc/Origin-Help/FIt-with-Err-Weight>). In subsection 3.2.3 dedicated to the THz monitoring of the ozone decay in CHARME, the error bars correspond also to the LODs estimated for all the measurements (each 3 min.) with the same method explained previously. We think that these error bars could be overestimated due to the batch processing.

According to this remark, the sentence has been rewritten:

*“The concentration decrease was fitted using the exponential law  $[O_3]_t = [O_3]_0 e^{-t/\tau_{O_3}}$ . A lifetime  $\tau_{O_3}$  of  $3.4 \pm 0.1 \text{ h}$  was deduced from a fit weighted on the instrumental errors corresponding here to LODs estimated with the same method as explained in the previous subsection with the Fig. 7b. In the present case, we can see that for ozone concentrations lower than 50 ppm, the lower error bars point to zero or negative values indicating that the LOD is reached as this level of concentration.”*

***L85. Depending on power and geometry of the fan system and depending on the nature of the reactive species being studied, the stirring of the gas mixture can lead to an increase of wall losses of the reactive species and not to a homogenization. I think this statement may require a reference concerning a study of the effect of the fans or should be phrased more carefully.***

The comment of RC1 (Line 85) is related to fan rotation speed, but in our experiments the fans were not activated. Indeed, the fans can only be used at atmospheric pressure (it is now mentioned in the section 2.1). However, we agree that the stirring of the gas mixture can lead to an increase of wall losses of the reactive species and not to a homogenization. This was observed in CHARME for secondary organic aerosols (see Fayad, 2019).

***L118. What kind of “static analysis” was performed? Finite element calculation? What conditions (force field) were assumed? Somewhat more detail is required here or an appropriate reference should be stated.***

The total deformation of the Chernin cell and the corresponding mounting flanges was analyzed under static conditions. The forces that were considered were their own gravity and the atmospheric pressure on the outer surface of the flanges when the chamber was in a vacuum state. This last sentence has been added in the revised text.

***L130. A pathlength of 540 m is claimed here, however, measurements are only shown up to 480 m.***

As shown in Fig. 3a, during the IR measurements, we succeeded to reach a pathlength of 540 m. corresponding to a matrix configuration of 9 rows and 6 columns (108 reflections) but the IR output power (around 50  $\mu\text{W}$ ) was not sufficient to detect the IR rovibrational line. In the manuscript, the longest IR pathlength is limited to 480 m. excepted for the power measurements (Fig. 3a). In the conclusion we also give an upper limit of 480 m. according to a 2<sup>nd</sup> remark of RC1.

***L134. Name the photodiode and give some specs. Ge, InGaAs? Bandwidth?  
Name the oscilloscope and give some specs (e.g. vertical resolution, sample rate, max frequency)***

We did it:

*“An InGaAs detector (Thorlabs PDA400) with a typical bandwidth of 10MHz was used for the detection. Spectra were obtained by applying a voltage ramp to the piezo actuator allowing an excursion of 0.17  $\text{cm}^{-1}$  around the line center of interest with a repetition rate of 1.3 Hz. The received photodiode signal was averaged by a digital oscilloscope (DSO-X 2002A Agilent Technologies, maximum frequency of 70MHz), the signal was typically accumulated over 16 ramp cycles with a sampling of 12.5 kHz (10 bits of vertical resolution).”*

***L164. How were the error bars determined?***

Here it is simply the error given by the fit. It is now mentioned in the text.

***Figure 3. I would plot a power law always in a double logarithmic graph rather than using linear axes. The right axes are missing in panels (a) and (b). Can the THz power fluctuations also be quantified?***

The figure 3 has been changed in order to provide both linear scale with the power law fit (in blue) and log scale with the linear fit (in red). Of course, both fits lead to the same reflectivity values. The THz error bars correspond to the measured power fluctuations.

***L179. Can more information be given on the code from LightMachinery Inc.?***

The web link is now given in the references.

**Figure 4 and L236.** *The unit on the ordinate of Fig. 4(b) and in Line 236 seems incorrect as far as the axis title is concerned. Depending on what variable the absorption coefficient is integrated over (frequency or wavenumber), the unit should not remain [cm<sup>-1</sup>], which is the unit of the absorption coefficient itself. What is probably meant here is the “integrated absorbance”, then the unit of [cm<sup>-1</sup>] is correct, if integrated over wavenumber.*

RC1 is right, we have used “the integrated absorbance” in cm<sup>-1</sup> unit and not the “the integrated absorption coefficient” which will be in cm<sup>-2</sup> unit. This mistake has been corrected all along the manuscript including the Y-axis labelling of Fig.4b and 5b. It answers also to reviewer for its remarks L.260.

**L236.** *Is the linear regression going through the origin or was it forced through zero? This is difficult to see in Figure 4(b). With a non-zero intercept the slope may change somewhat. Remedy: State the fit function explicitly.*

We have used a linear function and not an affine function for the fits in Fig. 4b and 5b. So yes the regression was forced through zero. It is now mentioned in the caption and the origins are now visible on Fig. 4b and 5b.

**Based on Figure 4(a) the estimated HWHM seems to be somewhat too small. FWHM seems to be more like ~0.028 cm<sup>-1</sup>.**

Here, we don't agree with RC1. As it was mentioned in the caption of the Fig. 4, the shoulder observed at low frequency is assigned to the ECDL source which is not perfectly monomode in this region. This shoulder does not belong to the probed rovibrational line and must not be taken into account in the rovibrational linewidth. This explains why we have this smaller linewidth compared to the value proposed by RC1.

**L241.** *The equation in that line requires more explanation. How was it derived? I find  $\alpha_{0,exp} = s \cdot \sqrt{\ln 2} / (\Delta \nu \cdot \sqrt{\pi})$ , if what was called “integrated absorption coefficient” is indeed “integrated absorbance”. If a HWHM of 0.014 cm<sup>-1</sup> is used this results in a similar value as stated, i.e.  $3.92 \times 10^{-6}$  cm<sup>-1</sup>. If the original HWHM is used one finds a value that is even larger, i.e.  $5.50 \times 10^{-6}$  cm<sup>-1</sup>.*

The book of M. Sigrist (Sigrist, 1994) was used as reference for the  $\alpha_{0,exp}$  equations. This reference is now added in the manuscript.  $\alpha_{0,exp}$  is in cm<sup>-1</sup> unit, it corresponds well to an absorption coefficient as it was mentioned previously by Reviewer1. We thank the reviewer1 for its remark and we have corrected the  $\alpha_{0,exp}$  expression for the near-IR measurements where the Doppler dominates the collisional broadening. So, in this case, we agree with reviewer1,  $\alpha_{0,exp} = s \cdot \sqrt{\ln 2} / (\Delta \nu \cdot \sqrt{\pi}) = 3.92 \times 10^{-6}$  cm<sup>-1</sup> with  $\Delta \nu = 0.014$  cm<sup>-1</sup> (HWHM).

**L265.** *How was  $\alpha_{0,exp}$  calculated here? A Voigt profile is used for the description of the absorbance of the measured line. What assumption was made?*

Compared to the Fig.4 where the near-IR where mainly Doppler broadened, the THz rotational lines in Fig.5 have a very small Doppler line-width (0.54 MHz HWHM). Therefore a Lorentzian profile is a good approximation and for this reason the absorption coefficient should be calculated with the relation  $\alpha_{0,exp} = s / (\Delta \nu \cdot \pi)$ . In the revised version of the manuscript we have updated Fig. 5b using now Lorentzian profiles to fit the absorbances shown in 5a. A linear fit without intercept is obtained from 120 m to 240 m. Compared to the previous version the slope is a little smaller but this small change does not modify the discussion.

***What would be of interest here also is to compare this value with the measured  $\alpha_{0,exp}$ , averaged for all 8 different pathlength measurements.***

Alpha<sub>0, exp</sub> is deduced from the fitted slopes determined in Fig. 4b & 5b, so the value takes into account the full set of measurements at different pathlengths.

***L.254. Where does the line intensity come from? How was this estimated? There is a reference needed here. It also says “experimentally measured”. By whom? In this work?***

The ground-state rotational lines of N<sub>2</sub>O in the millimeter-wave region are very well known. Line intensities are well determined thanks to a good knowledge of the permanent dipole moment of N<sub>2</sub>O. A very good line profile analysis on the same transition shown in Fig. 5 with the same kind of THz source was performed in 2005 by F. Rohart et al.. This reference is now added to the manuscript.

***L337: “...by fitting..” what? A ‘Voigt profile’? The function that is fitted to the data should be stated here (“...by fitting a Voigt profile...”). Moreover, in Figure 7 the absorbance spectrum of the R(22) of N<sub>2</sub>O line is shown. What do the authors mean by “integrated intensity” in Line 337?***

The rotational lines in Fig. 7 are fitted with a Voigt profile since at low pressure the Doppler and the collisional contributions of the broadening are rather close. The choice of the line profile is now stated in the manuscript. According to the remarks of reviewer 1, “integrated intensity” is replaced by “absorbance” L.337 and L.354.

***L338-342: It should be argued or shown that the “two baseline treatments” have no effect on the line shape and width. A comparison of results with and without the treatment could be shown here, since data manipulations like FFT filtering affect the line shape and hence the error of the resulting number density. A systematic error discussion could be included here.***

We have added a Fig. S5 in the Supplement describing the different steps of the post treatment used to reduce the oscillations due to standing waves occurring in MULTICHARME. It shows that only the rapid baseline oscillations are removed. The residual between raw and filtered data has an amplitude corresponding to around 5% of the total amplitude of the measured absorbance. With this figure, the reader can see that the line shape and the line width are preserved after the treatment. Now in the text we state that “*We have been careful that the post processing does not affect the line shape and hence the error of the resulting number density.*”

***Figure 7: Red and blue circles (or panels) seem to have been mixed up. It would be meaningful to show the fit residuals in panel below the main figures. The unit of the integrated absorbance is stated in MHz, however as per the main text (L344) this should be wavenumbers. Please be uniform in your notation.***

We don't understand why reviewer1 says that the *Red and blue circles (or panels) seem to have been mixed up?* Nevertheless, according to the remark of reviewer1, we propose a new Fig.7 with the fit residuals below the main figures. The fitted area in the caption are logically in MHz units according to the X-axes units in Fig.7. The conversion MHz → cm<sup>-1</sup> is required in a next step to determine the molecular density in molec/cm<sup>3</sup>.

***Since the concentrations in the current experiment are significantly higher it is not clear how meaningful this comparison to the work by Itoh et al. is. Itoh et al. measured from a pressure of 6.7 mbar, which is not even as low as in the present study it seems? The conditions in the present paper are typical for chamber cleaning activities. Under these conditions it is known that the O<sub>3</sub> loss in the chamber is dominated by wall reactions and not by reactions with O<sub>2</sub>. That is why these conditions are chosen to get rid of impurities, such as volatile organic compounds, on the chamber wall.***

***L406/407. Ozone being generated at atmospheric pressure? I thought the chamber was kept at low pressure in these experiments (see L375.)***

Itoh et al. have developed and experimentally verified a physical model allowing to understand the pressure and the wall material dependencies of the ozone-to-wall loss rate in a cylindrical tube (Itoh et al., 2004, 2011). In order to understand the differences between atmospheric pressure and low pressure measurements of the ozone lifetimes performed in CHARME, we thought it appropriate to mention the work of Itoh et al. even their low-pressure measurements are limited to few mbar. Effectively, the chamber was kept at low pressure during these experiments. Finally we converge to similar conclusions as RC1, so we have added at the end of section 3.2.3 the sentence proposed by RC1 in its report which allows to avoid any confusion: “*The pressure measurement conditions in THz rotational high-resolution spectroscopy are typical for chamber cleaning activities. Under these conditions it is known that the O<sub>3</sub> loss in the chamber is dominated by wall reactions and not by reactions with O<sub>2</sub>. It corresponds to the first term of Eq. (1) and, therefore, as it is shown by our results, a decrease of the lifetime at low pressure was expected due to the reinforcement of the losses by the ozone diffusion on the walls chamber. That is why these conditions are chosen to get rid of impurities, such as VOCs, on the chamber wall.*”

***All the other remarks of RC1 (mainly typographical) have been taken into account in the new version of the manuscript. All the propositions of RC1 concerning the references have been taken into account. The references have been completed and verified***